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Signed this 2nd day of April

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JaneMann

55697J.18 SPECIFICATION

The invention relates to the improvement in the dewaterability of biological clarified sludge having a dry content of more than 0.5% by weight, more particularly clarified sludge the solid content (dry matter) of which consists of at least 30% by weight of organic material. Clarified sludges of this kind come particularly from anaerobically operated digestion towers.

Prior art

In typical sewage clarifying works, first of all the coarse solids are allowed to settle out of the sewage arriving and these solids are separated off as a so-called primary sludge. The supernatant waste water is conveyed into a biological clarifying stage, where the dissolved and suspended solids are subjected to decomposition by microorganisms, either with ventilation or with the exclusion of air. The organic substance contained in the waste water is largely bound in the form of a mass of microorganisms. This is precipitated as a clarified sludge with a solids content of more than 0.5% by weight. The purified waste water can be released into rivers or allowed to seep away in sewage irrigation fields.

The clarified sludge must be dewatered until only a dry content remains which can be deposited. In many cases, the activated sludge obtained when air is admitted is subjected to treatment in a digestion tower under anaerobic conditions and the activated sludge is dewatered as it is. When dewatering is carried out on screen belt presses, decanters, chamber filter presses or the like, there is a problem that the biological

sludge, is difficult to dewater. The addition of flocculating agents to the activated sludge substantially speeds up the dewatering process and is therefore in general use. Using dewatering methods of this kind, sludges are obtained containing, for example, 27 to 30% by weight of solids, but a solids content of about 35% or more is needed for depositing. Therefore, the solids content is frequently increased by the addition of lime, which is disadvantageous, not only because of the lime needed but also because of the higher transporting weight and the increased space needed for depositing.

It is known to aid the biological clarification of sewage by the addition of enzymes. Thus, according to DE-A 24 24 116, enzymes are added to the sewage which have been obtained from microorganisms living in the water, the assumption being that a microorganism flora specific to the substrate will automatically form in the sewage. The enzymes are intended to accelerate the decomposition of the organic matter contained in the sewage and thereby make it possible for microorganisms to carry out the degradation.

The same purpose is served by the addition of enzymes such as lipases, amylases, cellulases or proteinases, to the effluent from slaughter-houses or other plants which produce waste water with a specific loading of fats, polysaccharides, proteins and the like, in the process according to DE-A 26 33 514. The degradation of the above-mentioned contents improves the dewaterability and the tendancy to sedimentation of these effluents.

In the Journal "Wochenblatt für Papierfabrikation" 1981, page 564, P. Dobianzki, C. H. Möbius and H.-H. Hofer discuss the possibility of reducing the protective colloid effect of starch by enzymatic decomposition of the starch in the circulating water used in paper

reducing the quantity of flocculant needed during clarification. Improved clarification properties were indeed achieved, but at the same time there were higher chemical and biological oxygen requirements, which were put down to the decomposition products and the amylase content.

In the processes described hereinbefore, the use of enzymes is intended directly to bring about the decomposition of the matter contained in the original sewage. For reasons of expense, these processes can only be considered for the treatment of special effluent which would be difficult to clarify in any other way. They do not solve the problem of improving the dewatering of biological clarified sludges. This latter purpose is served by a few enzymatic processes which will be described hereinafter.

According to DE-A 34 41 690, biological clarified sludge is treated with a chelating agent, such as nitrilotriacetic acid salts, and with enzymes and can then be reduced to 40% of its original volume.

In "Filtration & Separation", January 1979, pages 82-86, C. G. Carlson describes the treatment of aerobic bio-sludges with enzymes, particularly amylase, lipase and proteinase. These are intended in particular to decompose the extracellular sludges which surround the microorganisms contained in the biosludges and which contain the majority of the water which is difficult to separate off. The activity was found to depend more on the duration of the treatment than on the enzyme concentration. The filterability was significantly improved.

Objective and solution

The dewatering of biological clarified sludges with solids contents of more than 0.5% by weight, which can

enzyme preparations, is unsatisfactory and should be improved. This is achieved according to the invention by adding a synthetic organic flocculating agent after the action of the hydrolytic enzyme preparation.

The invention starts from the idea expressed by Carlson, namely that the extracellular slime of the microorganisms contained in the clarified sludge interfere with the dewatering. However, whereas Carlson was interested only in eliminating the water-retaining effect of these slimes in order to achieve sludges with a higher solids content, the inventors assume the inhibiting effect of the slimes on the flocculating process carried out with organic flocculating agents. Even though the invention is not tied to any particular theory, the findings can be interpreted as showing that the flocculation proceeds much more successfully after enzymatic attack on the slime. In any case, improved dewaterability of the sediment is achieved which goes far beyond the effect which could be ascribed to a reduction in the quantity of slime alone. In fact, this effect is demonstrated by comparative tests carried out without flocculating agent, with and without the use of enzyme.

This is hereinafter illustrated by the treatment of a number of samples of the same activated sludge with a solids content of 2.6% by weight taken from the digestion tower of a municipal clarification plant. The flocculating agent used was a high molecular copolymer of 30% acrylamide and 70% methacryloxyethyltrimethylammonium chloride. The enzyme used was a protease-rich preparation with optimum activity at pH 6 to 9. In each case, the sediment which had formed within 24 hours from the sludge, optionally after the addition of flocculating agent, was investigated. The dewaterability was determined using the standardised suction time (CST) according to the method described hereinafter: this specifies the time taken for the water

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sucked into a filter paper from a sample of sludge to spread to a certain extent. The shorter this time, the better the dewaterability.

Untreate	d sl	udge	2		*	CST	=	434	sec
sludge w				.of	enzyme	CST	=	372	sec
Sludge W	rith	2.1	g/kg	of	flocculating				
		ager				CST	=	54	sec
Sludge W	ith	2.1	g/kg	of	enzyme and				
		2.1	g/kg	of	flocculating				
		ager	nt			CST	=	30	sec

The effect of the enzyme alone reduces the CST by 14%. On the other hand, the CST is reduced by 44% when flocculating agent is added, under the effect of the enzyme.

Embodiment of the invention

The process according to the invention is suitable for treating all clarified sludges the dry matter of which consists to a considerable extent, sometimes more than half, of organic material. Typical dry contents of such clarified sludges are from 0.5 to 10, more particularly from 1 to 6% by weight. They are obtained in current methods of sewage treatment, particularly in anaerobically operating digestion towers. However, it is also possible to treat activated sludges from aerobically operated equipment.

As a rule, an organic polyelectrolyte is used as the synthetic organic flocculating agent. These flocculating agents are generally known in the clarification of sewage. Normally, they are high polymers with molecular weights (mean weight) of more than 500,000, more particularly more than 1 million. Preferred organic polyelectrolytes belong to the

covalently bound to the polymer molecule. Examples of cationic organic polyelectrolytes of this kind include polyethyleneimines and the salts thereof and polymers and copolymers of ethylenically unsaturated, radically polymerisable monomers with a secondary or tertiary amino group or a secondary, tertiary or quaternary ammonium salt group. The latter include in particular the tert.-aminoalkylesters and the tert.-aminoalkyl-amides of acrylic and methacrylic acid and the salts thereof with organic or, more particularly, inorganic acids and quaternisation products. Preferably, copolymers of acrylamide and a quaternised aminoalkylester of acrylic or methacrylic acid are used, the proportion of the latter preferably being in the range from 20 to 80% by weight.

The hydrolytic enzyme preparation used consists of industrial enzymes, generally obtained from microorganism cultures. They usually contain a spectrum of different enzyme activities. For the purposes of the invention it is advantageous to use enzyme preparations having high activities of carbohydrases, proteases, glycoproteinases and/or lipases. Of the carbohydrases, alpha-amylases, cellulases and beta-glucanases are the most important. It is also possible to mix together a number of industrial enzyme preparations in order to obtain a spectrum of activity of the desired breadth. Mixtures having amylases, cellulases and proteases as the main activities are preferred. For sludges obtained from municipal sewage, enzyme preparations with a high cellulase and/or hemicellulase activity have proved particularly suitable.

The quantity of hydrolytic enzyme preparation and synthetic flocculating agent used will depend on the properties of the sludge to be treated. It has been found that the properties of clarified sludges vary considerably, even when they are obtained from the same

in the method of treatment every day or several times a day. This may be connected with changes in the microorganism populations growing in the digestion tower and with the fluctuating arrival of certain ingredients in the waste water. The enzyme requirement is generally in the range from 0.001 to 10 g/kg of sludge. optimum quantity also depends on the dewatering method. The flocculating agent is generally used in a quantity of 0.02 to 300 g, preferably 25 to 150 g per 1000 litres of sludge. The metering of the two additives is preferably adjusted so that the CST is reduced by at least 10% and preferably by at least 15%, compared with the sludge treated only with flocculating agent. Although as a rule the effectiveness of the enzyme increases with the quantity used and the duration of the treatment, the reverse is occasionally found. Frequently, the effects of the enzyme preparation can be detected after a reaction time of only 2 hours. optimum reaction time is generally between 4 and 24 hours. The effects of the synthetic flocculating agent occur very rapidly, so that decanting or filtering can be carried out immediately after the addition of the flocculating agent.

Owing to the considerable fluctuations in qualities, it is advantageous to set up the operation of the clarification plant for rapid and frequent changes in the operating conditions. For this it is essential to have a method of testing which allows sampling to be carried out at short intervals; the CST method mentioned earlier is exceptionally suitable for this. Samples can be taken automatically, e.g. from a pipe through which the sludge is flowing, at fixed intervals of time and the CST can then be determined. An apparatus suitable for this purpose is described in German Utility Model G 87 01 550. When the CST increases, the automatic metering of the enzyme and/or flocculating agent can be

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An even more accurate adaptation to changes in the properties of the sludge is achieved if a larger number of sludge samples are taken one or more times a day and mixed with graduated amounts of different enzyme preparations of varying activity spectra and the CST is determined after different reaction times, in each case after the addition of flocculating agent. This testing can also be alternated and used for the automatic selection of the additive with the lowest CST.

The enzyme treatment is appropriately carried out in a container subjected to continuous flow and with a capacity corresponding to one or more days' throughput. Although it would be possible to adapt the pH of the sludge and the temperature thereof to the optimum activity of the enzyme preparation, the sludge is preferably subjected unchanged to the enzyme treatment. The pH is generally between 4.5 and 9 and the temperature is from 5 to 40°C, but in some cases it may be up to 75°C.

After the enzyme treatment the flocculating agent is preferably metered continuously into the flow of sludge, preferably in the form of a dilute aqueous solution. Further treatment in sedimentation tanks, decanters, screen belt presses and the like is carried out in the usual way. The sludge separated off has a solids content which is significantly higher than the level which can be achieved with flocculating agents alone and the possibility of depositing it is thereby improved. In typical cases, a solids content of more than thirty and preferably 35 or more percent is achieved with optimum treatment. In these cases, the sludge can be used directly for dumping.

Example 1

In a municipal clarifying plant, clarified sludge

The content of dry substance (TS) was 2.6%; the pH was 7.6.

One litre batches of the sludge were mixed with 0.21 or 2.1g/kg of sludge - TS of a microbially produced, protease rich enzyme preparation with an optimum pH from 6 to 8. The protease activity according to Löhlein-Volhard (cf "Das Leder", 1971, 22(6); 121f.) was 20,000 LVU/g. After reaction times of 4 and 24 hours at ambient temperature, the CST was measured with and without flocculating agents. The flocculating agent used was a commercially available cationic acrylamide copolymer (Rohafloc (R) KE 790 made by Rohm GmbH of Darmstadt) in a quantity of 2.1g/kg of sludge-TS. As a comparison, non-enzymatically treated sludge samples were used.

As shown in Table 1, the enzyme activity could still not be detected after four hours, but after 24 hours with and without the addition of flocculating agent a significantly lower CST was found. The CST was determined by a method described by U.Loll in "Korrespondenz Abwasser", 24th edition, 1977, pages 295-299. In this, a sludge sample is packed into a cylinder 18 mm wide which is sealed at the bottom with an absorbent filterboard disc. The latter absorbs water from the sample of sludge. The time taken for the circular area of absorbed water to extend from 32mm to 45mm in diameter is measured.

<u>Table l</u>		·	
Reaction	Metering of	Metering of	
Time	Enzyme	Flocculating	CST
(hours)	(g/kg TS)	Agent (g/kg TS)	(sec)
4	-	-	403.0 + 20.8
4	0.21	-	408.8 + 10.4
4	2.10	-	416.6 + 13.2
	٠		
24	-	-	434.1 + 16.7
24	0.21	-	418.0 + 10.5
24	2.10	- .	371.8 + 2.5
4	_	2.1	47.3 + 2.2
4	0.21	2.1	55.9 + 6.6
4	2.10	2.1	47.3 + 0.7
0.4	_	2.1	53.9 + 4.8
24	-	•	
24	0.21	2.1	48.8 + 4.6
24	2.10	2.1	29.7 + 3.8

Example 2

This was carried out analogously to Example 1 but at a different time. The somewhat different characteristics of the sludge can be put down to this. The sludge had a dry content of 2.5% TS and pH of 7.5.

The enzyme treatment was carried out using a microbially produced, amylase-rich enzyme product with an optimum pH 6 to 8 and an amylase activity of 10,000 SKB/g (according to Sandstedt, Kneen & Blish, "Cer. Chem", 1939, 16th edition, page 712). A reduction in the CST was detectable after only 4 hours enzyme treatment:

Table 2 Reaction Time (hours)	Metering of Enzyme (g/kg TS)	Metering of Flocculating Agent (g/kg TS)	CST (sec)
4	-	-	337.8 + 8.9
4	0.27	-	288.2 + 10.3
4	2.70	- .	334.5 + 14.3
24	-	-	344.6 + 0.6
24	0.27	-	324.2 + 13.7
24	2.70	-	341.7 + 20.8
4	-	2.1	100.5 + 9.3
4	0.27	2.1	63.1 + 4.4
4	2.70	2.1	65.2 + 5.4
24	-	2.1	68.0 + 5.6
24	0.27	2.1	42.5 + 1.2
24	2.70	2.1	55.6 + 3.5

The enzyme activities and dosages required for improved dewatering of the sludge are determined analogously to Examples 1 and 2 on sludge samples in the clarifying plant. The place of use of the enzymes in a municipal clarifying plant is illustrated in the diagram shown in Fig.1.

Primary sludge from the settling tank (1) of the stream of effluent is converted, either on its own or together with activated sludge from the aerobic biological clarifying stage (2, 2') in the digestion tower (3), into activated sludge, with the formation of methane. After a retention time of up to 3 weeks in the digestion tower, the sludge is thickened in a settling tank (4). The enzyme is metered in dissolved form into the connecting pipe (5) between the digestion tower (3)

therein. The retention time of up to 48 hours in the settling tank (4) is sufficient for the enzyme activity. The sludge flowing out is pumped to the dewatering plant (6) and dewatered after the addition of flocculating agents.

Example 3

This Example was carried out analogously to Examples 1 and 2 but at a different time. The dry content was 2.47% and the pH was 7.6. The enzyme used was microbially produced cellulase-rich enzyme product which also contains beta-glucanase, laminarinase and hemicellulase as secondary activities. The cellulase activity is 0.20 FPU/mg. The filter paper units (FPU) are determined according to M. Mandels, R. Andreotti and C. Roche in Biotechnol. Bioengin Symp. 6 (1976), 21 - 33 (Measurements of Saccharifying Cellulase).

This Example shows that both the CST values for enzyme-treated unflocculated sludge as well as flocculated sludge are improved substantially. The effect is achieved after only a few hours and is maintained for 24 hours. This is particularly important for the fluctuations which occur in practice in the retention times of the sludge in the thickener.

Table 3 Reaction Time (hours)	Metering of Enzyme (g/kg TS)	Metering of Flocculating Agent (g/kg TS)	CST (sec)	
4		_	379.3	H 4.3
4	0.22	_	335.6	10.6
4	2.15	-	310.3	9.4
24	-	-	351.2	
24	0.22	•	334.7	
24	2.15	-	314.8	10.5
4	-	2.2	76.8 -	+ 2.3
4	0.22	2.2	74.2	+ 4.4
4	2.15	2.2	45.3 -	+ 2.2
2.4	_	2.2	66.4	+ 5.5
24 24	0.22	2.2	65.6	+ 5.1
24	2.15	2.2	50.7	+ 6.3

Example 4

This Example was carried out in principle analogously to Examples 1 to 3 but at a different time. The measurement used for dewatering was the content of dry matter in the filter cake obtained by dewatering a sludge suspension with a compression permability cell (CP cell).

This consists of a piston and a cylinder which are pressed hydraulically together. Both the bottom of the cylinder and the top of the piston are covered by a filter cloth which is of the kind typically used for press filters. During the filling process, the CP cell stands in an upright position. The cylinder is filled with the sludge sample up to a desired initial cake

In order to ensure that the filtrate flows away at both sides, as in a chamber filter press, the CP cell is tilted into the horizontal position for the actual pressing operation. The filtrate flows through the filter cloth and a perforated plate below it into a filtrate collecting chamber and a collecting vessel.

a precisely selectable compression force.

For the enzyme treatment, a cellulase-rich enzyme product with a cellulase activity of 0.2 FPU/mg (filter paper units) was used.

The activated sludge (dry content 2.5%) was divided into samples of equal size. The enzyme concentration was 10 mg/litre of untreated sludge and the reaction time was 24 hours. From each batch of sludge, a zero sample is taken, to which no enzyme is added but which is also kept for 24 hours.

In the dewatering test, the CP cell is filled with two litres of the enzyme-treated, flocculated sludge. A cationic polyelectrolyte based on a methacrylic acid is used as the flocculating agent. The concentration of flocculating agent is 10g of flocculating agent of per kg of dry matter.

After a preliminary dewatering time of 6 minutes, in which the majority of the water in the sludge runs away under the effect of gravity filtration, the CP cell is moved up and tipped into a horizontal position. The remaining water is squeezed out by pressure filtration and a filter cake is obtained, the solids content of which is determined by drying.

Result:

After pressing, the dry content of the flocculated, non-enzyme treated sludge sample was 28.6%. A dry

Thus, the increase in the dry content as a result of enzyme treatment was 12.9%

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Claims

- 1. Process for improving the dewaterability of biological clarified sludge having a solids content of more than 0.5% by weight, in which a hydrolytic enzyme preparation is added to the clarified sludge, characterised in that, after this has acted, a synthetic organic flocculating agent is added.
- 2. Process according to claim 1, characterised in that a hydrolytic enzyme preparation is used which contains high activities of carbohydrases, proteases, glycoproteinases and/or lipases.
- 3. Process according to claim 2, characterised in that a hydrolytic enzyme preparation is used which contains high activities of amylases, cellulases and/or proteases.
- 4. Process according to claims 1 to 3, characterised in that an organic polyelectrolyte is used as the synthetic organic flocculating agent.
- 5. Process according to claim 4, characterised in that a cationic organic polyelectrolyte is used.
- 6. Process according to claim 5, characterised in that a copolymer of acrylamide and a quaternary aminoalkyl ester of acrylic or methacrylic acid is added as cationic organic polyelectrolyte.
- 7. Process according to claims 1 to 6 characterised in that the hydrolytic enzyme preparation and the synthetic flocculating agent are used in quantities such that the standardised suction time (CST) is reduced by at least 15% compared with sludge which has been treated only with the flocculating agent.

- 8. Process according to claims 1 to 7, characterised in that a clarified sludge is used, the solids content of which (dry substance) consists of at least 30% by weight of organic material.
- 9. Process according to claim 8, characterised in that the clarified sludge used is an activated sludge from an anaerobically operated activation tower.

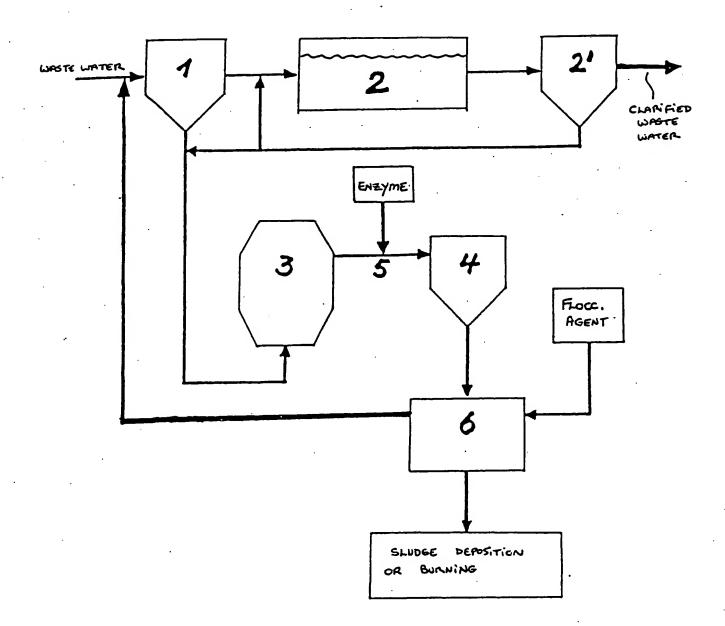


Fig. 1

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